**Laboratory Name:** Pacific Northwest National Laboratory
**B&R Code:** KC 020102

**FWP and/or subtask Title under FWP:**
Defects and Defect Processes in Ceramics

**FWP Number:** 18048

**Program Scope:**
Research integrates experimental, ab initio and computer simulation approaches to develop a fundamental understanding of and predictive models for equilibrium and non-equilibrium defect formation, migration, and interaction in ceramic materials. Ion channeling, electron microscopy, laser spectroscopies, and X-ray absorption spectroscopies are used to characterize defect properties, defect kinetics, irradiation-induced defect accumulation, phase transformations, and the evolution of nanoscale structures. Density functional theory and molecular dynamics methods are used to probe defect energetics and defect accumulation processes.

**Major Program Achievements (over duration of support):**
Quantified defect formation, defect migration, and amorphization processes in ceramics that contributed to development of new interatomic potentials for SiC, C, GaN, and $ZrSiO_4$. Contributed to understanding defect formation, defect stability and irradiation damage processes in GaN, $ZrSiO_4$, $SrTiO_3$, and $A_2B_2O_7$ pyrochlores. Discovered and verified by DFT that Ga implantation of GaN drives formation of a stable bridged 4-gallium atom structure with metallic bonding. Developed new models for irradiation-induced amorphization and disorder accumulation. Determined electronic stopping power in materials over continuous energy ranges for numerous ions.

**Program impact:**
Provided globally-adopted scientific insights, models, threshold displacement energies, and interaction potentials for ion-solid interactions and damage accumulation in ceramics. Provided a predictive model for radiation effects applicable to long-term storage of actinide-containing waste. Found that ion implanted graphite promotes fast pathways for H diffusion that has significant implications for reversible hydrogen storage applications.
(4 peer-reviewed book chapters, 81 peer-reviewed journal articles; 24 invited presentations Fy02-FY05)

**Interactions:**
Theory and computer simulations – L.R. Corrales, E.J. Bylaska (PNNL); C. Meis, A. Chartier, J.-P. Crocombette (CEA-Saclay, France); M. Posselt (Research Center Rossendorf, Germany); H. Jónsson (University of Washington); L.W. Hobbs (MIT); T.J. Lenosky (Ohio State University); P. Sigmund (Odense University, Denmark)

Experimental Studies – R.C. Ewing and L.M. Wang (University of Michigan); A. Hallén (Royal Institute of Technology, Sweden); L.A. Boatner (ORNL); B.D. Begg (Australian Nuclear Science & Technology Organization); G. Possnert (University of Uppsala, Sweden); M. Higuchi (Hokkaido University, Japan)

**Recognitions, Honors and Awards (at least in some part attributable to support under this program):**
W.J. Weber: Chair/Co-Chair, Workshop on Theory and Computer Simulations of Radiation Effects in Ceramics; Workshop on Radiation Effects in Complex Ceramics; International Conference on Alternative Nuclear Wasteforms; International Conference on Alternative Nuclear Waste Forms; International Conference on Radiation Effects in Insulators; MRS Symposium on Growth, Modification, and Analysis by Ion Beams at the Nanoscale; International Conference on Computer Simulation of Radiation Effects in Solids. International Committee Member for: Radiation Effects in Insulators; Computer Simulations of Radiation Effects in Solids; Radiation Effects in Insulators. Principal Editor and Editorial Board member: Journal of Materials Research. Editorial Board: Nuclear Instruments and Methods in Physics Research, Section B. R. Devanathan**:** Co-Chair, MS&T-2006 Symposium on Radiation Effects in Materials; MRS Symposium on Multiscale Modeling of Materials.

**Personnel Commitments for FY2005 to Nearest +/- 10%:**
W.J. Weber (40%), F. Gao (50%), W. Jiang (90%), R. Devanathan (50%), Y. Zhang (40%), H.L. Heinisch (25%)

**Authorized Budget (BA) for FY03, FY04, FY05:**
**FY03 BA** $758k **FY04 BA** $859k **FY05 BA** $825k

**Laboratory Name:** Pacific Northwest National Laboratory
**B&R Code:** KC020105

**FWP and/or subtask Title under FWP:**
Chemistry and Physics of Ceramic Surfaces

**FWP Number:** 10122

**Program Scope:**
The role of resident defects in altering physical properties of materials is probed through an integrated experimental-theoretical approach where relationships among processing parameters, ensuing structure and attendant properties are sought. Molecular approaches to deposit textured thin films and targeted atom bonding arrangements are pursued that yield surfaces with site specificity for chemical reactions, unique ion and charge transport properties, and remarkable magnetic behavior. Results provide the basic understanding necessary to design, deposit, and modify thin films with specific properties. Research underpins a broad range of critical technologies ranging from transport of electron spin and charge across interfaces to sequestration and reactivity of molecules at tailored interfaces.

**Major Program Achievements (over duration of support):**
(1) A definitive correlation has been made between resident structure and room-temperature ferromagnetism in magnetically doped $TiO_2$ epitaxially deposited films of unsurpassed quality and solution-derived nanoparticles. (2) Exceptional polaron-driven conductivity was discovered in certain nickel/cobalt spinel oxides that is promoted by resident disorder within the cation lattice. (3) A pioneering Reactive Ballistic Deposition (RBD) method for synthesizing ulta-high surface area nanoporous oxide materials has been developed. (4) A new method based on cryogenic physisorption was pursued to quantify adsorbate binding to and desorption from defect sites on oxide surfaces. (5) A mathematical inversion procedure was developed in order to extract quantitative coverage dependent adsorption energies from temperature programmed desorption spectra. (6) Molecular beam techniques were used to study the activated dissociation of $CH_4$ on Pd nanoclusters supported on MgO(100).

**Program Impact:**
The role of surface adsorbed water on planarizing thin metal film overlayers empowers the development of next generation magnetic memories, and more cost effective catalytic materials. In a paradigm-breaking discovery, evidence unequivocally shows that defect-free ferromagnetic semiconductors are not intrinsically ferromagnetic, but rather paramagnetic; ferromagnetism originates from attendant chemical and structural defects. Highly conductive transition metal spinel oxides are under investigation as candidate electrode materials for solid oxide fuel cells.

**Interactions:**
Internal - Institute for Interfacial Catalysis, Fundamental Science Directorate, Environmental and Molecular Sciences Laboratory, Materials Science Division, JIN (Joint Institute of Nanotechnology – PNNL & UW.
External - UW, (Deposition, Characterization, Modeling), UT (molecule/surface interactions); UF (electronic structure modeling); SNL (modeling surface adsorbed water); BNL (electronic structural calculations and photoemission measurements using synchrotron radiation), APS User Facility (XAS measurements); Hewlett Packard ($CH_3OH$ and $H_2O$ adsorption on titania); Tulane University (Molecular adsorption on surfaces).

**Recognitions, Honors and Awards (at least in some part attributable to support under this program):**
S.A. Chambers: E.W. Muller Award, Fellow AVS; G.J. Exarhos: Editor – VACUUM, AVS Publications Chair, AVS/Surface Engineering Executive Committee, Fellow (ACerS, AVS, AAAS), B.D. Kay: DOE/BES Council of Chemical Sciences, BES Materials Sciences Division Committee of Visitors, Fellow (AVS, APS, AAAS); Editorial Board Member (Progress in Surface Science, Journal of Physical Chemistry, Vice Chair Elect, Vice Chair (ACS).
27 invited presentations, 5 invited articles, 37 publications, 2 patents

**Personnel Commitments for FY2005 to Nearest +/- 10%:**
S.A. Chambers (50%), Z. Dohnalek (40%), T.C. Droubay (30%). L.-Q. Wang (30%), K.F. Ferris (20%), B.D. Kay (20%), G.J. Exarhos (10%)

**Authorized Budget (BA) for FY03, FY04, FY05:**
**FY03 BA** $523k **FY04 BA $639**k **FY05 BA** $589k

**Laboratory Name:** Pacific Northwest National Laboratory
**B&R Code:** KC020105

**FWP and/or Subtask Title under FWP:**
Molecularly Organized Nanostructural Materials

**FWP Number:** 12152

**Program Scope:**
Synthesis approaches are designed to achieve targeted nano-porous-architectures through molecular control of chemical reactivity at interfaces. Solution templating routes, usually involving biological templates based upon carbohydrates, invoke structure-directing properties of chemically tailored surfactants or copolymers to induce ordering through mediation of hydrophilic and hydrophobic interactions of precursor reagents. Related modeling and simulation studies probe the stability of molecular conformations and generate guidelines for predicting structural change. Characterization approaches rely heavily on non-conventional magnetic resonance and optical spectroscopic methods that are augmented by electron microscopy, and both neutron and x-ray scattering methods.

**Major Program Achievements (over duration of support):**
(1) The order in which two fundamental assembly mechanisms occur in floppy molecules (intramolecular molecule folding and intermolecular self-assembly) determines the architecture of the evolving structure.
(2) Solution-driven surfactant templating approaches followed by pyrolysis in the absence of air replicates structures of natural products (e.g., wood, pollen, rice hulls) over all length scales (nm to mm) in metal carbides such as SiC.
(3) Temperature-dependent, continuous flow hyperpolarized (HP) $^{129}$Xe NMR probes pore structure and interconnectivity in high surface area mesoporous materials including aerogels or mineralized wood in analogy to the Temperature Programmed Desorption measurement used to quantify molecular adsorption at surfaces.
(4) Hydrothermal treatment of aqueous sugar solution yields uniform, porous carbon nanospheres by a condensation mechanism where the evolving hydrophobic phase is partitioned from the slowly dehydrating sugar molecules.

**Program Impact:**
Temperature dependent xenon magnetic resonance measurements are a superior probe of micro- and meso- porosity and pore interconnectivity in high surface area materials that supplement structural information available from neutron and x-ray scattering. Mineralization of wood and conversion to other ceramic phases opens the road to extremely robust catalyst support materials, and high surface area matrices/filters for waste and toxic material sequestration. Manipulation of both intra- and inter- molecular forces is key to development of smart materials that respond reversibly to changes in the ambient environment for sensors and actuators. Computational molecular design yields structure/property relationships that guide synthesis of materials having a predetermined response.

**Interactions:**
Internal—Fundamental Science Directorate, Environmental and Molecular Sciences Laboratory, Institute for Interfacial Catalysis; External— Project Coordinator, DOE CSP (Smart Materials Based on Electroactive Polymers), LLNL (ICF target development), LANL (aerogel nanoporosity), SNL (polymer ordering, templated self-assembly in solution), NRC-Canada (HP Xe NMR determination of porosity), Clemson University (solution-derived composite materials), WSU (molecular self-assembly), PSU (CP-MAS Solid State NMR & theoretical simulations).

**Recognitions, Honors and Awards (at least in some part attributable to support under this program):**
G.J Exarhos: Society Fellow (ACerS, AVS, AAAS); Editor, VACUUM; Member, AVS Long Range Planning; AVS Publications Chair; AVS Surface Engineering Division Executive Committee; A.D-Q Li: Beckman Young Investigator Award, NIH General Medicine (GM) RO1 Award. (35 publications, 16 invited talks, 2 patents)

**Personnel Commitments for FY2005 to Nearest +/- 10%:**
G.J. Exarhos (50%), W.D. Samuels (30%), Y. Shin (60%), L.-Q. Wang (50%), C.F. Windisch, Jr. (30%) A. DeQuan Li (WSU) (30%)

**Authorized Budget (BA) for FY03, FY04, FY2005:**
**FY03 BA $** 661k **FY04 BA $** 760k **FY05 BA $** 732k